The *Si*-2,4,6-Trimethoxyphenyl Moiety as a Novel Protecting Group in Organosilicon Chemistry: Alternative Synthesis of *rac*-Sila-venlafaxine

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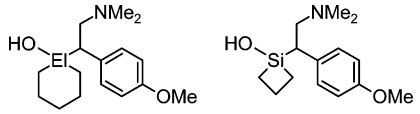
The *Si*-2,4,6-trimethoxyphenyl (*Si*-2,4,6-TMOP) moiety is claimed to be an effective protecting group for synthetic organosilicon chemistry. To demonstrate its high synthetic potential, the *Si*-2,4,6-TMOP protecting group has been used for a novel multistep synthesis of *rac*-sila-venlafaxine (a sila-analogue of the serotonin/noradrenaline reuptake inhibitor *rac*-venlafaxine), starting from 1,1-dichloro-1-silacyclohexane. In addition, the *Si*-2,4,6-TMOP moiety has been used as a protecting group in silacyclobutane chemistry.

Introduction

As demonstrated in a recently published review, organosilicon chemistry is broadly accepted as a novel source of chemical diversity in drug design.[1] Eight silicon-containing drugs have entered human clinical trials, and two further organosilicon compounds are in widespread use as agrochemical pesticides.[1] In this context, the development of new synthetic methods in organosilicon chemistry is very challenging. In particular, there is a need for broadly applicable silicon-bound protecting groups that allow a variety of chemical transformations at silicon-bound substituents and that finally can be removed easily to give reactive SiX groups (X = halogen, OR, NR_2, H).

In context with our systematic studies on silicon-based drugs (for some recent examples, see ref 2), we have recently synthesized *rac*-sila-venlafaxine (*rac*-**1b**), a sila-analogue of the serotonin/noradrenaline reuptake inhibitor *rac*-venlafaxine (*rac*-**1a**).[2i] We report here on an alternative synthesis of *rac*-**1b** and on the attempted synthesis of the derivative *rac*-**2** using the *Si*-2,4,6-trimethoxyphenyl (*Si*-2,4,6-TMOP) moiety as a protecting group. The aim of this study was to evaluate the synthetic potential of this particular protecting group for organosilicon chemistry. (2,4,6-Trimethoxyphenyl)-silanes have been synthesized and studied before,[3] but these studies were not aimed at the development of the *Si*-2,4,6-TMOP moiety as a protecting group, except for one recent application developed by our group.[3f]



1a: El = C
1b: El = Si

2

Results and Discussion

Syntheses. *rac*-Sila-venlafaxine (*rac*-**1b**) was synthesized according to Scheme 1 in a multistep synthesis in 21% or 27% (without isolation of **6**) overall yield, starting from 1,1-dichloro-1-silacyclohexane[2i] (**3**). Thus, reaction of **3** with 1 molar equiv of (2,4,6-trimethoxyphenyl)lithium, followed by methanolysis of the remaining Si−Cl bond, yielded 1-methoxy-1-(2,4,6-trimethoxyphenyl)-1-silacyclohexane (**4**) (yield 66%). Treatment of **4** with [1-(4-methoxyphenyl)vinyl]lithium gave 1-[1-(4-methoxyphenyl)vinyl]-1-(2,4,6-trimethoxyphenyl)-1-silacyclohexane (**5**) (yield 47%), which in turn was used to prepare 1-chloro-1-[1-(4-methoxyphenyl)vinyl]-1-silacyclohexane (**6**) (yield 77%) by treatment with an ethereal hydrogen chloride solution (selective cleavage of the *Si*-2,4,6-TMOP protecting group; no side products arising from cleavage of the other Si−C bonds could be detected by GC-MS analysis). Reaction of **6** with dimeth-

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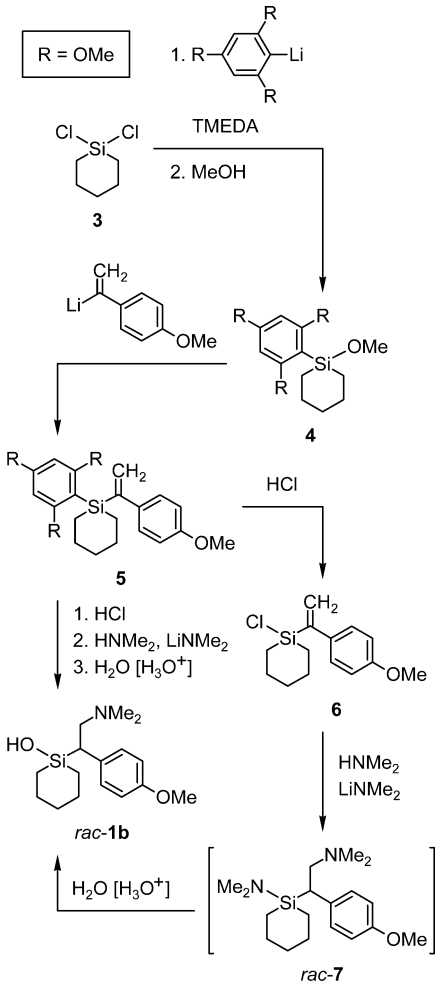
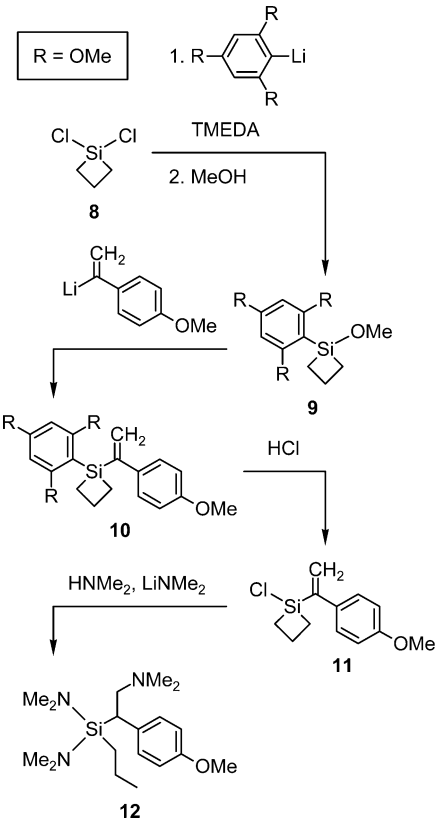
Scheme 1



Scheme 2



ylamine/lithium dimethylamide, followed by hydrolysis, finally afforded *rac*-**1b** (yield 86%). Alternatively, *rac*-**1b** was prepared directly from **5** by treatment with an ethereal hydrogen chloride solution (no isolation of the resulting chlorosilane **6**), followed by reaction with dimethylamine/lithium dimethylamide and subsequent hydrolysis (yield 86%). In the transformation **6** → *rac*-**1b**, *rac*-1-(dimethylamino)-1-[2-(dimethylamino)-1-(4-methoxyphenyl)ethyl]-1-silacyclohexane (*rac*-**7**) was shown to be an intermediate (comparison with an authentic sample;[2i] GC-MS analysis).

The strategy that has been established for the preparation of *rac*-**1b** (Scheme 1) was also applied to the synthesis of the derivative *rac*-**2** (Scheme 2). Thus, treatment of 1,1-dichloro-1-silacyclobutane (**8**) with 1 molar equiv of (2,4,6-trimethoxyphenyl)lithium, followed by methanolysis of the remaining Si−Cl bond, afforded 1-methoxy-1-(2,4,6-trimethoxyphenyl)-1-silacyclobutane (**9**) (yield 58%). Treatment of **9** with [1-(4-methoxyphenyl)vinyl]lithium gave 1-[1-(4-methoxyphenyl)-vinyl]-1-(2,4,6-trimethoxyphenyl)-1-silacyclobutane (**10**) (yield 62%), which in turn was used to prepare 1-chloro-1-[1-(4-methoxyphenyl)vinyl]-1-silacyclobutane (**11**) (yield 53%) by treatment with an ethereal hydrogen chloride solution (selective cleavage of the *Si*-2,4,6-TMOP protecting group; no side products arising from cleavage of the other Si−C bonds could be detected by GC-MS analysis). Subsequent treatment of **11** with dimethylamine/lithium dimethylamide (analogous to the transformation **6** → *rac*-**1b**) surprisingly afforded bis(dimethylamino)[2-(dimethylamino)-1-(4-methoxyphenyl)-ethyl]propylsilane (**12**) (yield 57%); i.e., in addition to the attempted chloro/dimethylamino exchange at the silicon atom and the amine addition to the vinyl group, ring opening (Si−C cleavage) of the silacyclobutane skeleton took place. This ring opening, which can be explained by the higher ring strain compared to that of the silacyclohexane skeleton, prevented the synthesis of *rac*-**2** by this route.

Compounds *rac*-**1b**, **4**, **5**, **9**, and **10** were isolated as colorless crystalline solids, whereas **6**, **11**, and **12** were obtained as colorless liquids. The identities of all these compounds were established by elemental analyses and NMR studies (^{1}H, ^{13}C, ^{29}Si), and **4**, **5**, and **10** were additionally characterized by crystal structure analyses.

Crystal Structure Analyses. Compounds **4**, **5**, and **10** were structurally characterized by single-crystal X-ray diffraction. The crystal data and the experimental parameters used for these studies are given in Table 1. The molecular structures of **4**, **5**, and **10** are depicted in Figures 1−3; selected interatomic distances and bond angles are given in the respective figure captions.

Compounds **4** and **5** exhibit approximately tetrahedral coordination at their silicon atoms, whereas the Si-coordination polyhedron of **10** is a strongly distorted tetrahedron. This distortion is forced by the geometry of the four-membered silacyclobutane ring, which adopts a butterfly conformation. The silacyclohexane rings of **4** and **5** are characterized by a chair conformation. The bond lengths and angles of **4**, **5**, and **10** are in the expected range and therefore do not need further discussion.

Compounds **4**, **5**, and **10** exhibit short intramolecular distances between the silicon atoms and the oxygen

Table 1. Crystal Data and Experimental Parameters for the Crystal Structure Analyses of 4, 5, and 10

	4	5	10
empirical formula	$C_{15}H_{24}O_4Si$	$C_{23}H_{30}O_4Si$	$C_{21}H_{26}O_4Si$
formula mass, g mol^{-1}	296.43	398.56	370.51
collection T, K	173(2)	173(2)	173(2)
λ(Mo Kα), Å	0.71073	0.71073	0.71073
cryst syst	orthorhombic	triclinic	monoclinic
space group (No.)	$P2_12_12_1$ (19)	$P\bar{1}$ (2)	$P2_1/n$ (14)
a, Å	6.7418(6)	8.3831(12)	12.3183(15)
b, Å	12.8308(14)	9.2713(12)	7.3965(11)
c, Å	18.615(3)	28.720(4)	21.489(3)
α, deg	90	95.090(16)	90
β, deg	90	95.010(17)	97.044(15)
γ, deg	90	100.338(16)	90
V, Å^3	1610.3(3)	2175.1(5)	1943.1(4)
Z	4	4	4
D(calcd), g cm^{-3}	1.223	1.217	1.267
μ, mm^{-1}	0.156	0.133	0.144
F(000)	640	856	792
cryst dimens, mm	0.5 × 0.15 × 0.07	0.4 × 0.4 × 0.4	0.5 × 0.5 × 0.3
2θ range, deg	5.40−52.74	5.02−56.04	5.82−52.84
index ranges	$-8 \le h \le 7$, $-16 \le k \le 15$, $-21 \le l \le 23$	$-11 \le h \le 11$, $-12 \le k \le 11$, $-37 \le l \le 37$	$-15 \le h \le 15$, $-9 \le k \le 9$, $-26 \le l \le 26$
no. of collected rflns	7361	20 546	26 008
no. of indep rflns	3241	9605	3959
R_{int}	0.0475	0.0700	0.0483
no. of rflns used	3241	9605	3959
no. of params	185	513	239
S^a	0.914	1.083	1.058
weight parameters a/b^b	0.0305/0.0000	0.0452/1.0800	0.0627/0.4654
$R1^c$ ($I > 2\sigma(I)$)	0.0354	0.0501	0.0376
$wR2^d$ (all data)	0.0710	0.1376	0.1073
absolute structure param	0.06(14)		
max/min residual electron density, e Å^{-3}	+0.185 /−0.191	+0.386/−0.299	+0.317/−0.232

[a] $S = \{\sum[w(F_o^2 - F_c^2)^2]/(n - p)\}^{0.5}$; n = no. of reflections, p = no. of parameters. [b] $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$, with $P = [\max(F_o^2,0) + 2F_c^2]/3$. [c] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [d] $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{0.5}$.

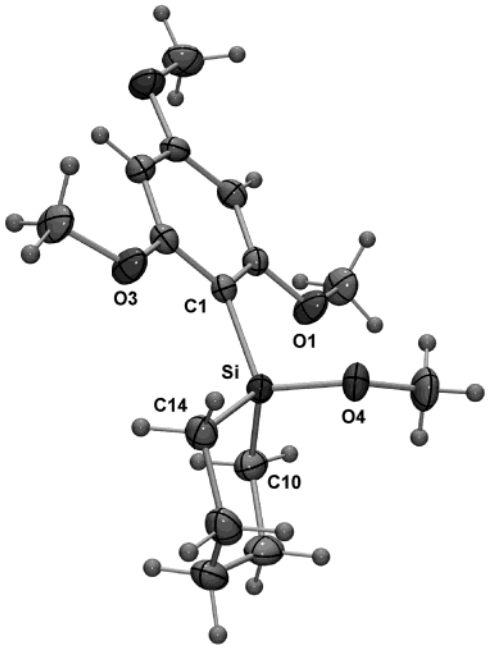


Figure 1. Molecular structure of **4** in the crystal (probability level of displacement ellipsoids 50%). Selected interatomic distances (Å) and bond angles (deg): Si−C1 = 1.888(2), Si−C10 = 1.867(2), Si−C14 = 1.864(2), Si−O4 = 1.6509(14), Si···O1 = 2.9001(16), Si···O3 = 3.1189(15); C1−Si−C10 = 111.92(10), C1−Si−C14 = 115.04(10), C1−Si−O4 = 110.07(8), C10−Si−C14 = 104.35(11), C10−Si−O4 = 110.54(9), C14−Si−O4 = 104.56(9).

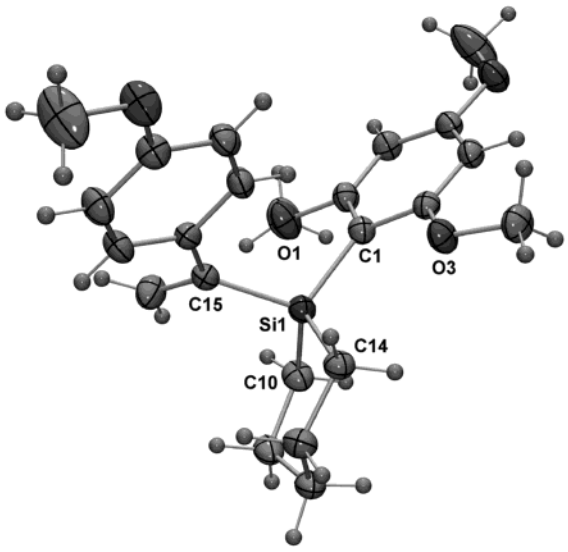


Figure 2. Molecular structure of one of the two crystallographically independent molecules in the crystal of **5** (probability level of displacement ellipsoids 50%). Selected interatomic distances (Å) and bond angles (deg): Si1−C1 = 1.8838(19), Si1−C10 = 1.8890(19), Si1−C14 = 1.881(2), Si1−C15 = 1.8903(19), Si1···O1 = 2.9037(17), Si1···O3 = 3.1249(15); C1−Si1−C10 = 110.62(9), C1−Si1−C14 = 113.44(9), C1−Si1−C15 = 111.16(8), C10−Si1−C14 = 104.01(9), C10−Si1−C15 = 109.80(9), C14−Si1−C15 = 107.52(9). The structure of the other molecule is very similar.

atoms in the *o*-methoxy groups. These Si···O distances are all shorter than the sum of the van der Waals radii of silicon (2.1 Å) and oxygen (1.5 Å) but significantly longer than a typical covalent Si−O bond (1.64 Å)[4] of a tetracoordinate silicon compound. The Si···O distances

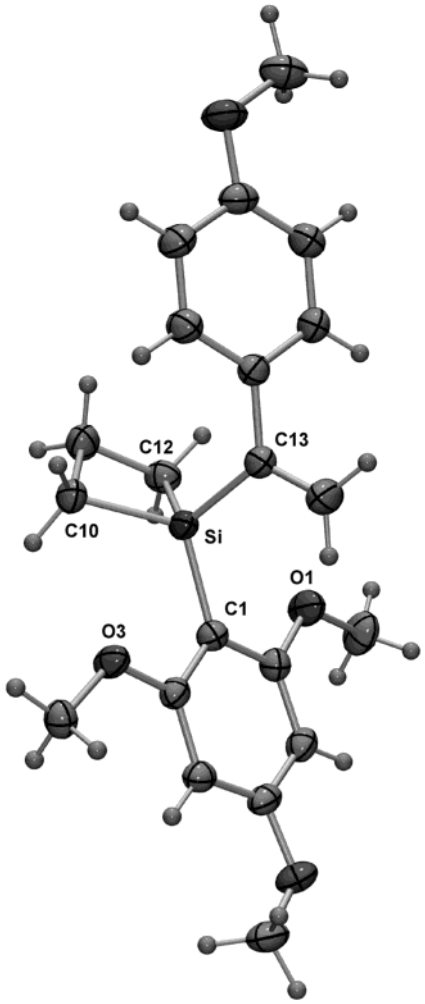


Figure 3. Molecular structure of **10** in the crystal (probability level of displacement ellipsoids 50%). Selected interatomic distances (Å) and bond angles (deg): Si−C1 = 1.8681(13), Si−C10 = 1.8829(14), Si−C12 = 1.8803(14), Si−C13 = 1.8850(14), Si···O1 = 2.9226(11), Si···O3 = 3.0136(10); C1−Si−C10 = 118.49(6), C1−Si−C12 = 120.79(6), C1−Si−C13 = 109.26(6), C10−Si−C12 = 79.00(6), C10−Si−C13 = 115.73(6), C12−Si−C13 = 110.96(6).

fall in the range 2.90−3.12 Å, each *Si*-2,4,6-TMOP group exhibiting one shorter and one longer Si···O contact. Very similar results have been reported for a series of other (2,4,6-trimethoxyphenyl)silanes.[3e]

Conclusions

We have demonstrated the *Si*-2,4,6-TMOP moiety to be an effective protecting group for synthetic organosilicon chemistry. It fulfills all the major requirements that have been claimed to be necessary for a good protecting group:[5] (i) the reagents for its introduction and cleavage are commercially available; (ii) its introduction is easy and effective and does not lead to additional stereogenic centers; (iii) it is easy to characterize (^{1}H and ^{13}C NMR spectroscopy); (iv) it is stable to a wide range of workup and reaction conditions, including chromatography on silica gel; (v) it can be removed efficiently and selectively; (vi) the byproduct of the deprotection (1,3,5-trimethoxybenzene) can be separated easily from the substrate.

In addition to the above-mentioned profile, there are two additional points: (vii) (2,4,6-trimethoxyphenyl)-silanes exhibit a high tendency for crystallization, making their isolation, purification, and characterization (crystal structure analysis) very easy; (viii) they have low UV detection limits.

The Si−C cleavage of the *Si*-2,4,6-TMOP moiety has been demonstrated to occur with hydrogen chloride in diethyl ether at 0 °C, without use of any catalyst (such as $AlCl_3$), to yield a chlorosilane. The *Si*-allyl group and other *Si*-aryl moieties have also been reported to be removable by Si−C cleavage; however, these cleavage reactions have been accomplished with triflic acid[2k,6] or trifluoroacetic acid.[7] Thus, the easily and selectively removable *Si*-2,4,6-TMOP group complements the toolbox of protecting groups in organosilicon chemistry that can be removed by acid-induced Si−C cleavage.

The use of the *Si*-2,4,6-TMOP moiety as a protecing group in silacyclobutane chemistry is of special interest: (i) (2,4,6-trimethoxyphenyl)lithium reacts selectively (monosubstitution) with 1,1-dichloro-1-silacyclobutane; (ii) the presence of the bulky *Si*-2,4,6-TMOP group does not render the *Si*-methoxy group in compound **9** unreactive, thus allowing the transformation **9** → **10**; (iii) most importantly, the *Si*-2,4,6-TMOP group can be cleaved selectively with hydrogen chloride from the silacyclobutane ring (transformation **10** → **11**) without any other Si−C bond cleavage. This is especially remarkable, as numerous Si−C bond cleavage reactions with hydrogen chloride, leading to ring opening of the silacyclobutane backbone, have been reported in the literature.[8]

Experimental Section

General Procedures. Except for the hydrolysis *rac*-**7** → *rac*-**1b**, all syntheses were carried out under dry nitrogen. The organic solvents used were dried and purified according to standard procedures and stored under dry nitrogen. A Büchi GKR 50 apparatus was used for the bulb-to-bulb distillations. Melting points were determined with a Büchi Melting Point B-540 apparatus using open glass capillaries. The ^{1}H, ^{13}C, and ^{29}Si NMR spectra were recorded on a Bruker DRX-300 NMR spectrometer (^{1}H, 300.1 MHz; ^{13}C, 75.5 MHz; ^{29}Si, 59.6 MHz).

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$CDCl_3$, CD_2Cl_2, and [D_8]THF were used as the solvents. All spectra were recorded at 22 °C. Chemical shifts were determined relative to internal $CHCl_3$ (^{1}H, δ 7.24; $CDCl_3$), $CDCl_3$ (^{13}C, δ 77.0; $CDCl_3$), $CHDCl_2$ (^{1}H, δ 5.32; CD_2Cl_2), CD_2Cl_2 (^{13}C, δ 53.8; CD_2Cl_2), [D_7]THF (^{1}H, δ 1.73; [D_8]THF), [D_8]THF (^{13}C, δ 25.3; [D_8]THF), or external TMS (^{29}Si, δ 0; $CDCl_3$, CD_2Cl_2, [D_8]THF). Assignment of the ^{1}H NMR data was supported by ^{1}H,^{1}H and ^{13}C,^{1}H correlation experiments, and assignment of the ^{13}C NMR data was supported by DEPT 135 and ^{13}C,^{1}H correlation experiments. The $^2J_{HH}$ coupling constants reported for the C=CH_2 groups represent absolute values.

Preparation of *rac*-1-[2-(Dimethylamino)-1-(4-methoxyphenyl)ethyl]-1-silacyclohexan-1-ol (*rac*-Sila-venlafaxine, *rac*-1b). Method A. A 2.5 M solution of *n*-butyllithium in *n*-hexane (4.2 mL, 10.5 mmol of *n*-BuLi) was added dropwise at −50 °C within 2 min to a stirred solution of dimethylamine (6.91 g, 153 mmol) in tetrahydrofuran (THF) (20 mL). The resulting mixture was warmed to −25 °C within 90 min and then cooled to −40 °C, followed by dropwise addition of a solution of **6** (1.35 g, 5.06 mmol) in THF (8 mL) within a period of 4 min. The stirred mixture was warmed to −20 °C within 2 h and then stirred at 0 °C for a further 1 h (complete conversion **6** → *rac*-**7**; GC control). Subsequently, the mixture was warmed to 20 °C within 1 h, and the solvent was removed under reduced pressure at 5−15 °C until a residual volume of ca. 10 mL was obtained. This solution was diluted with diethyl ether (20 mL) and then added in one single portion at 0 °C to a stirred two-phase mixture of diethyl ether (10 mL) and 2 M potassium acetate/acetic acid buffer (pH 4.5, 50 mL). The pH of the aqueous phase changed to pH 5.7 within ca. 10 min and was readjusted to pH 5.0 by addition of small portions of glacial acetic acid. The mixture was stirred at 0 °C for a further 1 h, with the pH of the aqueous phase remaining constantly at pH 5.0 during this time. The aqueous layer was separated, the organic phase was extracted with 1 M potassium acetate/acetic acid buffer (pH 5.0, 3 × 20 mL), and the aqueous solutions were combined. Diethyl ether (20 mL) was added to the combined aqueous extracts, and the pH of the aqueous phase was adjusted to pH 10.5 by addition of small portions of a saturated aqueous potassium carbonate solution. The organic layer was separated, the aqueous phase was extracted with diethyl ether (4 × 20 mL), and the organic extracts were combined, followed by addition of *n*-hexane (80 mL). The solvent was removed under reduced pressure at 5−15 °C until a residual volume of ca. 50 mL was obtained, whereupon residual water separated from the organic phase (formation of a two-phase system). The organic layer was separated, the aqueous phase was extracted with *n*-hexane (2 × 15 mL), and the organic solutions were combined. The solvent was removed completely under reduced pressure at 5−15 °C to give a colorless oil, which was dried in vacuo (0.001 mbar, 20 °C, 1 h) and then crystallized from *n*-pentane (25 mL; crystallization at −26 °C over a period of 3 days) using seed crystals.[2i] The product was isolated by quick decantation of the cold solvent, followed by drying in vacuo (0.001 mbar, 20 °C, 6 h) to give *rac*-**1b** in 86% yield as a colorless crystalline solid (1.27 g, 4.33 mmol); mp 33 °C. ^{1}H NMR ($CDCl_3$): δ 0.44−0.78, 1.00−1.15, and 1.19−1.69 (m, 10 H, Si(CH_2)$_5$), 2.29 (s, 6 H, NCH_3), 2.44 (δ_C), 2.52 (δ_A), and 3.12 (δ_B) (3 H, $^2J_{AB}$ = −12.1 Hz, $^3J_{AC}$ = 5.0 Hz, $^3J_{BC}$ = 12.1 Hz, SiCH_CCH_ACH_BN), 3.75 (s, 3H, OCH_3), 5.6 (br s, 1 H, SiO*H*), 6.75−6.83 (m, 2 H, *H*-3/*H*-5, $C_6H_4OCH_3$), 6.91−6.98 (m, 2 H, *H*-2/*H*-6, $C_6H_4OCH_3$). ^{13}C NMR ($CDCl_3$): δ 12.1 (SiCH_2C), 14.2 (SiCH_2C), 24.06 (SiCH$_2$CH_2C), 24.13 (SiCH$_2$CH_2C), 29.4 (Si(CH$_2$)$_2$CH_2C), 32.6 (SiCHC$_2$), 45.4 (NCH_3), 55.2 (OCH_3), 61.8 (NCH_2C), 113.8 (*C*-3/*C*-5, $C_6H_4OCH_3$), 128.2 (*C*-2/*C*-6, $C_6H_4OCH_3$), 133.0 (*C*-1, $C_6H_4OCH_3$), 157.1 (*C*-4, $C_6H_4OCH_3$). ^{15}N NMR ($CDCl_3$): δ −353. ^{29}Si NMR ($CDCl_3$): δ 10.3. Anal. Calcd for $C_{16}H_{27}NO_2Si$: C, 65.48; H, 9.27; N, 4.77. Found: C, 65.6; H, 9.5; N, 4.7.

Method B. Solution A: a 2.0 M ethereal hydrogen chloride solution (12.5 mL, 25.0 mmol of HCl) was added to a solution of **5** (9.39 g, 23.6 mmol) in diethyl ether (25 mL) in a single portion at 0 °C, and the resulting mixture was stirred at 0 °C for 10 min (complete conversion **5** → **6**; GC control). The solvent and the excess hydrogen chloride were removed under reduced pressure at 5−15 °C, and the oily residue was dried in vacuo (0.001 mbar, 20 °C, 10 min) and then dissolved in THF (25 mL). Solution B: a 2.5 M solution of *n*-butyllithium in *n*-hexane (20.0 mL, 50.0 mmol of *n*-BuLi) was added dropwise at −50 °C within 10 min to a stirred solution of dimethylamine (13.7 g, 304 mmol) in THF (50 mL). The resulting mixture was warmed to −10 °C within 2 h.

Solution B was then cooled to −40 °C, followed by dropwise addition of Solution A within a period of 4 min. The resulting stirred mixture was warmed to −20 °C within 2 h and then stirred at 0 °C for a further 2 h (complete conversion **6** → *rac*-**7**; GC control). Subsequently, the solution was warmed to 20 °C within 1 h, and the solvent was removed under reduced pressure at 5−15 °C until a residual volume of ca. 35 mL was obtained. This solution was diluted with diethyl ether (50 mL) and then added in a single portion at 0 °C to a stirred two-phase mixture of diethyl ether (50 mL) and 2 M potassium acetate/acetic acid buffer (pH 4.5, 100 mL). The pH of the aqueous phase changed to pH 6.0 within ca. 10 min and was readjusted to pH 5.0 by addition of small portions of glacial acetic acid. The mixture was stirred at 0 °C for a further 1 h, with the pH of the aqueous phase remaining constantly at pH 5.0 during this time. The aqueous layer was separated, the organic phase was extracted with 1 M potassium acetate/acetic acid buffer (pH 5.0, 3 × 50 mL), and the aqueous solutions were combined and then extracted with diethyl ether (100 mL). The aqueous layer was separated, the organic phase was extracted with 1 M potassium acetate/acetic acid buffer (pH 5.0, 2 × 50 mL), and the aqueous solutions were combined. Diethyl ether (100 mL) was added to the combined aqueous extracts, and the pH of the aqueous phase was adjusted to pH 10.5 by addition of small portions of a saturated aqueous potassium carbonate solution. The organic layer was separated, the aqueous phase was extracted with diethyl ether (5 × 150 mL), and the organic extracts were combined, followed by addition of *n*-hexane (200 mL). The solvent was removed under reduced pressure at 5−15 °C until a residual volume of ca. 150 mL was obtained, whereupon residual water separated from the organic phase (formation of a two-phase system). The organic layer was separated, the aqueous phase was extracted with *n*-hexane (2 × 50 mL), and the organic solutions were combined. The solvent was removed completely under reduced pressure at 5−15 °C to give a colorless oil, which was dried in vacuo (0.001 mbar, 20 °C, 1 h) and then crystallized from *n*-pentane (110 mL; crystallization at −26 °C over a period of 3 days) using seed crystals.[2i] The product was isolated by quick decantation of the cold solvent, followed by drying in vacuo (0.001 mbar, 20 °C, 6 h) to give *rac*-**1b** in 86% yield as a colorless crystalline solid (5.98 g, 20.4 mmol); mp 33 °C. Anal. Calcd for $C_{16}H_{27}NO_2Si$: C, 65.48; H, 9.27; N, 4.77. Found: C, 65.4; H, 9.1; N, 4.7. For NMR data, see Method A.

Preparation of 1,1-Dichloro-1-silacyclohexane (3). This compound was prepared according to ref 2i.

Preparation of 1-Methoxy-1-(2,4,6-trimethoxyphenyl)-1-silacyclohexane (4). A suspension of 1,3,5-trimethoxybenzene (50.0 g, 297 mmol) in a mixture of *n*-hexane (175 mL) and 1,2-bis(dimethylamino)ethane (TMEDA; 35.7 g, 307 mmol) was heated to ca. 50 °C to dissolve the 1,3,5-trimethoxybenzene. After the heat source was removed, a 2.5 M solution of *n*-butyllithium in *n*-hexane (121 mL, 303 mmol of *n*-BuLi) was added dropwise within 30 min to the vigorously stirred mixture. During the addition, the heat of reaction caused the mixture to boil under reflux, and a white precipitate was formed. After the addition was complete, the mixture was stirred vigorously (to prevent agglomeration) at 20 °C for 3 days (formation of (2,4,6-trimethoxyphenyl)lithium), and the resulting suspension was then added via a dropping funnel

at 0 °C within 20 min to a vigorously stirred solution of **3** (50.3 g, 297 mmol) in *n*-hexane (150 mL). The mixture was stirred at 0 °C for a further 15 min and then at 20 °C for 6 h, followed by dropwise addition of methanol (13.1 g, 409 mmol) within a period of 5 min (warming to ca. 30−40 °C; formation of a precipitate). The stirred mixture was cooled to 20 °C within 1 h and then stirred at this temperature for a further 16 h. The resulting suspension was filtered, the filter cake was washed with *n*-hexane (2 × 300 mL), and the filtrate and wash solutions were combined. The solvent was removed under reduced pressure, and the liquid residue was distilled in vacuo (Kugelrohr apparatus; first fraction, ≤120 °C/0.001 mbar, discarded; second fraction, 120−170 °C/0.001 mbar, crude product (65.2 g of a colorless liquid)). The crude product was redistilled in vacuo (Vigreux column, 10 cm) to give **4** in 66% yield as a colorless oily liquid (58.3 g, 197 mmol); bp 105 °C/0.001 mbar. After the liquid was kept at 15−20 °C for 7 days, it solidified to give a colorless crystalline solid; mp 24−25 °C. ^{1}H NMR (CD_2Cl_2): δ 0.75−0.89, 1.08−1.20, 1.23−1.35, 1.53−1.67, and 1.73−1.87 (m, 10 H, Si(CH_2)$_5$), 3.41 (s, 3 H, SiOCH_3), 3.73 (s, 6 H, *o*-OCH_3, $C_6H_2(OCH_3)_3$), 3.81 (s, 3 H, *p*-OCH_3, $C_6H_2(OCH_3)_3$), 6.07 (s, 2 H, *H*-3/*H*-5, $C_6H_2(OCH_3)_3$). ^{13}C NMR (CD_2Cl_2): δ 16.0 (SiCH$_2$C), 25.0 (SiCH$_2$CH$_2$C), 30.4 (Si(CH$_2$)$_2$CH$_2$C), 50.8 (SiOCH_3), 55.4 (*o*-OCH_3, $C_6H_2(OCH_3)_3$), 55.5 (*p*-OCH_3, $C_6H_2(OCH_3)_3$), 90.5 (*C*-3/*C*-5, $C_6H_2(OCH_3)_3$), 102.9 (*C*-1, $C_6H_2(OCH_3)_3$), 164.2 (*C*-4, $C_6H_2(OCH_3)_3$), 167.3 (*C*-2/*C*-6, $C_6H_2(OCH_3)_3$). ^{29}Si NMR (CD_2Cl_2): δ 2.5. Anal. Calcd for $C_{15}H_{24}O_4Si$: C, 60.78; H, 8.16. Found: C, 60.7; H, 7.8.

Preparation of 1-[1-(4-Methoxyphenyl)vinyl]-1-(2,4,6-trimethoxyphenyl)-1-silacyclohexane (5). A 2.5 M solution of *n*-butyllithium in *n*-hexane (75.0 mL, 188 mmol of *n*-BuLi) was added dropwise at −78 °C within 20 min to a stirred mixture consisting of finely ground 4-methoxyacetophenone 2,4,6-triisopropylbenzenesulfonylhydrazone[2i] (40.0 g, 92.9 mmol), TMEDA (31.0 g, 267 mmol), and *n*-hexane (300 mL). The resulting yellow mixture was stirred at −78 °C for 2 h and then warmed to 0 °C within 90 min (evolution of nitrogen; change of color to orange; formation of [1-(4-methoxyphenyl)-vinyl]lithium)). After the nitrogen evolution had finished, the resulting clear solution was stirred at 20 °C for a further 10 min and then added dropwise at 20 °C within 25 min to a solution of **4** (27.5 g, 92.8 mmol) in *n*-hexane (200 mL). During the addition, the mixture was warmed to ca. 30 °C. The solution was then cooled to 20 °C and stirred at this temperature for 16 h (change of color from orange to yellow), followed by the addition of silica gel (50 g; 32−63 μm, ICN 02826). The resulting suspension was shaken for 2 min and then subjected to flash chromatography (column diameter, 5.5 cm; column length, 50 cm; silica gel, 520 g (32−63 μm, ICN 02826); the silica gel that was added before shaking the mixture was allowed to form a sediment on the top of the column in this step), using petroleum ether (40−65 °C)/diethyl ether/triethylamine (55:40:5 (v/v/v)) as the eluent. The relevant fraction that contained the crude product was concentrated under reduced pressure, the liquid residue was distilled in vacuo (Kugelrohr apparatus; first fraction, ≤160 °C/0.001 mbar, discarded; second fraction, 160−220 °C/0.001 mbar, crude product (31.3 g of a colorless liquid)), and the crude product was crystallized from *n*-hexane (120 mL; crystallization at −20 °C over a period of 3 days). The resulting product was isolated by decantation, washed with cold (−20 °C) *n*-pentane (10 mL), recrystallized from *n*-hexane (90 mL; crystallization at −20 °C over a period of 4 days), washed with cold (−20 °C) *n*-pentane (10 mL), and dried in vacuo (0.001 mbar, 20 °C, 2 h) to give **5** in 47% yield as a colorless crystalline solid (17.5 g, 43.9 mmol); mp 45−46 °C. ^{1}H NMR (CD_2Cl_2): δ 1.05−1.13, 1.26−1.41, and 1.43−1.78 (m, 10 H, Si(CH_2)$_5$), 3.70 (s, 6 H, *o*-OCH_3, $C_6H_2(OCH_3)_3$), 3.76 (s, 3 H, *p*-OCH_3, $C_6H_4OCH_3$), 3.80 (s, 3 H, *p*-OCH_3, $C_6H_2(OCH_3)_3$), 5.65 (δ_A) and 5.88 (δ_B) ($^2J_{AB}$ = 3.2 Hz, 2 H, C=CH_AH_B), 6.08 (s, 2 H, *H*-3/*H*-5, $C_6H_2(OCH_3)_3$), 6.73−6.79 (m, 2 H, *H*-3/*H*-5, $C_6H_4OCH_3$), 7.13−7.19 (m, 2 H, *H*-2/*H*-6, $C_6H_4OCH_3$). ^{13}C NMR (CD_2Cl_2): δ 15.0 (SiCH$_2$C), 25.2 (SiCH$_2$CH$_2$C), 30.6 (Si(CH$_2$)$_2$CH$_2$C), 55.37 (*o*-OCH_3, $C_6H_2(OCH_3)_3$), 55.44 (*p*-OCH_3, $C_6H_2(OCH_3)_3$, or *p*-OCH_3, $C_6H_4OCH_3$), 55.5 (*p*-OCH_3, $C_6H_2(OCH_3)_3$, or *p*-OCH_3, $C_6H_4OCH_3$), 90.8 (*C*-3/*C*-5, $C_6H_2(OCH_3)_3$), 103.6 (*C*-1, $C_6H_2(OCH_3)_3$), 113.5 (*C*-3/*C*-5, $C_6H_4OCH_3$), 126.2 (C=*C*H$_2$), 128.1 (*C*-2/*C*-6, $C_6H_4OCH_3$), 137.7 (*C*-1, $C_6H_4OCH_3$), 150.4 (*C*=CH$_2$), 158.6 (*C*-4, $C_6H_4OCH_3$), 164.0 (*C*-4, $C_6H_2(OCH_3)_3$), 167.0 (*C*-2/*C*-6, $C_6H_2(OCH_3)_3$). ^{29}Si NMR (CD_2Cl_2): δ −15.4. Anal. Calcd for $C_{23}H_{30}O_4Si$: C, 69.31; H, 7.59. Found: C, 69.1; H, 7.5.

Preparation of 1-Chloro-1-[1-(4-methoxyphenyl)vinyl]-1-silacyclohexane (6). A 2.0 M ethereal hydrogen chloride solution (11.5 mL, 23.0 mmol of HCl) was added to a solution of **5** (8.70 g, 21.8 mmol) in diethyl ether (30 mL) in a single portion at 0 °C, and the resulting mixture was stirred at 0 °C for 10 min (complete conversion **5** → **6**, GC control). The solvent and the excess hydrogen chloride were removed under reduced pressure at 5−15 °C, the oily residue was dried in vacuo (0.001 mbar, 20 °C, 1 h) and dissolved in *n*-hexane (40 mL), and the resulting solution was then kept undisturbed at −20 °C for 2 days (crystallization of 1,3,5-trimethoxybenzene). The precipitate was separated by filtration and washed with cold (−20 °C) *n*-hexane (20 mL), the filtrate and wash solution were combined, and the solvent was removed under reduced pressure at 5−15 °C. The oily residue was distilled in vacuo (Vigreux column, 5 cm) to give **6** in 77% yield as a colorless liquid (4.46 g, 16.7 mmol); bp 120−122 °C/0.001 mbar. ^{1}H NMR ($CDCl_3$): δ 0.87−1.02, 1.05−1.17, 1.19−1.34, and 1.57−1.92 (m, 10 H, Si(CH_2)$_5$), 3.79 (s, 3 H, OCH_3), 5.73 (δ_A) and 6.00 (δ_B) ($^2J_{AB}$ = 2.2 Hz, 2 H, C=CH_AH_B), 6.82−6.89 (m, 2 H, *H*-3/*H*-5, $C_6H_4OCH_3$), 7.23−7.30 (m, 2 H, *H*-2/*H*-6, $C_6H_4OCH_3$). ^{13}C NMR ($CDCl_3$): δ 15.7 (SiCH$_2$C), 23.5 (SiCH$_2$CH$_2$C), 29.2 (Si(CH$_2$)$_2$CH$_2$C), 55.2 (OCH_3), 113.8 (*C*-3/*C*-5, $C_6H_4OCH_3$), 128.0 (*C*-2/*C*-6, $C_6H_4OCH_3$), 129.0 (C=*C*H$_2$), 134.2 (*C*-1, $C_6H_4OCH_3$), 147.1 (*C*=CH$_2$), 158.9 (*C*-4, $C_6H_4OCH_3$). ^{29}Si NMR ($CDCl_3$): δ 14.7. Anal. Calcd for $C_{14}H_{19}ClOSi$: C, 63.02; H, 7.18. Found: C, 62.9; H, 7.2.

1,1-Dichloro-1-silacyclobutane (8). This compound was commercially available (ABCR/Gelest, SIC2568.0)

Preparation of 1-Methoxy-1-(2,4,6-trimethoxyphenyl)-1-silacyclobutane (9). A suspension of 1,3,5-trimethoxybenzene (57.2 g, 340 mmol) in a mixture of *n*-hexane (200 mL) and TMEDA (40.0 g, 344 mmol) was heated to ca. 50 °C to dissolve the 1,3,5-trimethoxybenzene. After the heat source was removed, a 2.5 M solution of *n*-butyllithium in *n*-hexane (138 mL, 345 mmol of *n*-BuLi) was added dropwise within 30 min to the vigorously stirred mixture. During the addition, the heat of reaction caused the mixture to boil under reflux, and a white precipitate was formed. After the addition was complete, the mixture was stirred vigorously (to prevent agglomeration) at 20 °C for 3 days (formation of (2,4,6-trimethoxyphenyl)lithium), and the resulting suspension was then added via a dropping funnel at 0 °C within 30 min to a vigorously stirred solution of **8** (48.0 g, 340 mmol) in *n*-hexane (150 mL). The mixture was stirred at 0 °C for a further 15 min and then at 20 °C for 3 h, followed by dropwise addition of methanol (12.7 g, 396 mmol) within a period of 5 min (warming to ca. 30−40 °C; formation of a precipitate). The stirred mixture was cooled to 20 °C within 1 h and then stirred at this temperature for a further 5 h. The resulting suspension was filtered, the filter cake was washed with *n*-hexane (200 mL) and resuspended in *n*-hexane (250 mL), and the resulting mixture was heated under reflux for 5 min and filtered in the heat. The filter cake was washed again with *n*-hexane (100 mL), and all the filtrates and wash solutions were combined. The solvent was removed under reduced pressure, and the liquid residue was distilled in vacuo (Kugelrohr apparatus; first fraction, ≤145 °C/0.001 mbar, discarded; second fraction, 145−165 °C/0.001 mbar, crude product (57.1 g of a colorless solid)). The solid distillate was recrystallized from boiling *n*-hexane (300 mL; crystallization at 4 °C over a period of

16 h) to give **9** in 58% yield as a colorless crystalline solid (53.1 g, 198 mmol); mp 76−77 °C. ^{1}H NMR (CD_2Cl_2): δ 1.31−1.55 (m, 4 H, SiCH_2C), 1.66−2.00 (m, 2 H, CCH_2C), 3.49 (s, 3 H, SiOCH_3), 3.75 (s, 6 H, *o*-OCH_3, $C_6H_2(OCH_3)_3$), 3.82 (s, 3 H, *p*-OCH_3, $C_6H_2(OCH_3)_3$), 6.09 (s, 2 H, *H*-3/*H*-5, $C_6H_2(OCH_3)_3$). ^{13}C NMR (CD_2Cl_2): δ 15.3 (CCH_2C), 20.2 (SiCH_2C), 51.0 (SiOCH_3), 55.6 (*o*-OCH_3, $C_6H_2(OCH_3)_3$), 55.8 (*p*-OCH_3, $C_6H_2(OCH_3)_3$), 90.6 (*C*-3/*C*-5, $C_6H_2(OCH_3)_3$), 102.7 (*C*-1, $C_6H_2(OCH_3)_3$), 164.8 (*C*-4, $C_6H_2(OCH_3)_3$), 166.9 (*C*-2/*C*-6, $C_6H_2(OCH_3)_3$). ^{29}Si NMR (CD_2Cl_2): δ 7.7. Anal. Calcd for $C_{13}H_{20}O_4Si$: C, 58.18; H, 7.51. Found: C, 58.1; H, 7.4.

Preparation of 1-[1-(4-Methoxyphenyl)vinyl]-1-(2,4,6-trimethoxyphenyl)-1-silacyclobutane (10). A 2.5 M solution of *n*-butyllithium in *n*-hexane (75.0 mL, 188 mmol of *n*-BuLi) was added dropwise at −78 °C within 20 min to a stirred mixture consisting of finely ground 4-methoxyacetophenone 2,4,6-triisopropylbenzenesulfonylhydrazone[2i] (40.0 g, 92.9 mmol), TMEDA (31.0 g, 267 mmol), and *n*-hexane (300 mL). The resulting yellow mixture was stirred at −78 °C for 2 h and then warmed to 0 °C within 90 min (evolution of nitrogen; change of color to orange; formation of [1-(4-methoxyphenyl)-vinyl]lithium). After the nitrogen evolution had finished, the resulting clear solution was stirred at 20 °C for a further 10 min and then added dropwise within 25 min to a gently refluxing[9] solution of **9** (24.9 g, 92.8 mmol) in *n*-hexane (200 mL). The solution was then cooled to 20 °C and stirred at this temperature for 16 h (change of color from orange to yellow), followed by the addition of silica gel (50 g; 32−63 μm, ICN 02826). The resulting suspension was shaken for 2 min and then subjected to flash chromatography (column diameter, 5.5 cm; column length, 50 cm; silica gel, 520 g (32−63 μm, ICN 02826); the silica gel that was added before shaking the mixture was allowed to form a sediment on the top of the column in this step), using petroleum ether (40−65 °C)/diethyl ether/triethylamine (55:40:5 (v/v/v)) as the eluent. The relevant fraction that contained the crude product was concentrated under reduced pressure, the liquid residue was distilled in vacuo (Kugelrohr apparatus; first fraction, ≤180 °C/0.001 mbar, discarded; second fraction, 180−200 °C/0.001 mbar, crude product (21.9 g of a yellowish oily liquid)), and the crude product was crystallized from *n*-hexane (145 mL; crystallization at 4 °C over a period of 3 days). The resulting product was isolated by decantation, washed with cold (4 °C) *n*-pentane (10 mL), and dried in vacuo (0.001 mbar, 20 °C, 2 h) to give **10** in 62% yield as a colorless crystalline solid (21.3 g, 57.5 mmol); mp 45−46 °C. ^{1}H NMR (CD_2Cl_2): δ 1.31−1.54 (m, 4 H, SiCH_2C), 1.92−2.23 (m, 2 H, CCH_2C), 3.72 (s, 6 H, *o*-OCH_3, $C_6H_2(OCH_3)_3$), 3.77 (s, 3 H, *p*-OCH_3, $C_6H_4OCH_3$), 3.80 (s, 3 H, *p*-OCH_3, $C_6H_2(OCH_3)_3$), 5.73 (δ_A) and 6.03 (δ_B) ($^2J_{AB}$ = 2.8 Hz, 2 H, C=CH_AH_B), 6.08 (s, 2 H, *H*-3/*H*-5, $C_6H_2(OCH_3)_3$), 6.77−6.84 (m, 2 H, *H*-3/*H*-5, $C_6H_4OCH_3$), 7.31−7.39 (m, 2 H, *H*-2/*H*-6, $C_6H_4OCH_3$). ^{13}C NMR (CD_2Cl_2): δ 16.9 (SiCH_2C), 19.2 (CCH_2C), 55.5 (*p*-OCH_3, $C_6H_2(OCH_3)_3$, or *p*-OCH_3, $C_6H_4OCH_3$), 55.6 (*p*-OCH_3, $C_6H_2(OCH_3)_3$, or *p*-OCH_3, $C_6H_4OCH_3$), 55.7 (*o*-OCH_3, $C_6H_2(OCH_3)_3$), 90.8 (*C*-3/*C*-5, $C_6H_2(OCH_3)_3$), 103.9 (*C*-1, $C_6H_2(OCH_3)_3$), 113.7 (*C*-3/*C*-5, $C_6H_4OCH_3$), 125.4 (C=CH_2), 128.1 (*C*-2/*C*-6, $C_6H_4OCH_3$), 135.9 (*C*-1, $C_6H_4OCH_3$), 149.7 (*C*=CH_2), 158.9 (*C*-4, $C_6H_4OCH_3$), 164.4 (*C*-4, $C_6H_2(OCH_3)_3$), 166.3 (*C*-2/*C*-6, $C_6H_2(OCH_3)_3$). ^{29}Si NMR (CD_2Cl_2): δ 1.4. Anal. Calcd for $C_{21}H_{26}O_4Si$: C, 68.07; H, 7.07. Found: C, 68.1; H, 7.2.

Preparation of 1-Chloro-1-[1-(4-methoxyphenyl)vinyl]-1-silacyclobutane (11). A 2.0 M ethereal hydrogen chloride solution (10.0 mL, 20.0 mmol of HCl) was added to a solution of **10** (7.24 g, 19.5 mmol) in diethyl ether (25 mL) in a single portion at 0 °C, and the resulting mixture was stirred at 0 °C for 10 min (complete conversion **10** → **11**, GC control). The solvent and the excess hydrogen chloride were removed under reduced pressure at 5−15 °C, the oily residue was dried in vacuo (0.001 mbar, 20 °C, 1 h) and dissolved in *n*-hexane (35 mL), and the resulting solution was then kept undisturbed at −20 °C for 2 days (crystallization of 1,3,5-trimethoxybenzene). The precipitate was separated by filtration and washed with cold (−20 °C) *n*-hexane (20 mL), the filtrate and wash solution were combined, and the solvent was removed under reduced pressure at 5−15 °C. The oily residue was distilled in vacuo (Vigreux column, 5 cm) to give **11** in 53% yield as a colorless liquid (2.48 g, 10.4 mmol); bp 93−95 °C/0.001 mbar. ^{1}H NMR ($CDCl_3$): δ 1.59−1.67 (m, 4 H, SiCH_2C), 1.94−2.11 and 2.19−2.37 (m, 2 H, CCH_2C), 3.80 (s, 3 H, OCH_3), 5.83 (δ_A) and 6.17 (δ_B) ($^2J_{AB}$ = 1.8 Hz, 2 H, C=CH_AH_B), 6.85−6.92 (m, 2 H, *H*-3/*H*-5, $C_6H_4OCH_3$), 7.29−7.36 (m, 2 H, *H*-2/*H*-6, $C_6H_4OCH_3$). ^{13}C NMR ($CDCl_3$): δ 16.0 (CCH_2C), 20.3 (SiCH_2C), 55.2 (OCH_3), 114.0 (*C*-3/*C*-5, $C_6H_4OCH_3$), 127.76 (*C*-2/*C*-6, $C_6H_4OCH_3$), 127.83 (C=CH_2), 132.5 (*C*-1, $C_6H_4OCH_3$), 146.6 (*C*=CH_2), 159.2 (*C*-4, $C_6H_4OCH_3$). ^{29}Si NMR ($CDCl_3$): δ 21.0. Anal. Calcd for $C_{12}H_{15}ClOSi$: C, 60.36; H, 6.33. Found: C, 60.2; H, 6.4.

Preparation of Bis(dimethylamino)[2-(dimethylamino)-1-(4-methoxyphenyl)ethyl]propylsilane (12). A 2.5 M solution of *n*-butyllithium in *n*-hexane (8.7 mL, 21.8 mmol of *n*-BuLi) was added dropwise at −50 °C within 10 min to a stirred solution of dimethylamine (6.05 g, 134 mmol) in THF (20 mL). The resulting mixture was warmed to −10 °C within 2 h and then cooled to −40 °C, followed by dropwise addition of a solution of **11** (2.48 g, 10.4 mmol) in THF (8 mL) within a period of 10 min. The stirred mixture was warmed to −20 °C within 2 h and then to 20 °C within 4 h and was stirred at 20 °C for a further 10 h (complete conversion **11** → **12**; GC control). The mixture was then cooled to 0 °C, chlorotrimethylsilane (2.32 g, 21.4 mmol) was added in a single portion, and the resulting mixture was stirred at 0 °C for 30 min. The solvent was removed under reduced pressure at 5−15 °C, *n*-hexane (20 mL) was added, and the mixture was stirred at 20 °C for 10 min (formation of a precipitate). The mixture was filtered, the filter cake was washed with *n*-hexane (10 mL), the filtrate and wash solutions were combined, the solvent was removed under reduced pressure, and the residue was distilled in vacuo (Vigreux column, 5 cm) to give **12** in 57% yield as a colorless liquid (1.99 g, 5.89 mmol); bp 112−115 °C/0.001 mbar. ^{1}H NMR ([D$_8$]THF): δ 0.28−0.50 (m, 2 H, SiCH_2C), 0.88 (t, $^3J_{HH}$ = 7.2 Hz, 3 H, CCH_3), 1.19−1.44 (m, 2 H, CCH_2C), 2.06 (s, 6 H, CNCH_3), 2.44 (s, 6 H, SiNCH_3), 2.47 (s, 6 H, SiNCH_3), 2.55 (δ_A), 2.59 (δ_X), and 2.81 (δ_B) ($^2J_{AB}$ = −13.0 Hz, $^3J_{AC}$ = 3.0 Hz, $^3J_{BC}$ = 12.2 Hz, 3 H, SiCH_CCH_ACH_BN), 3.71 (s, 3 H, OCH_3), 6.71−6.78 (m, 2 H, *H*-3/*H*-5, $C_6H_4OCH_3$), 6.93−7.00 (m, 2 H, *H*-2/*H*-6, $C_6H_4OCH_3$). ^{13}C NMR ([D$_8$]THF): δ 16.4 (SiCH_2C), 17.7 (CCH_2C), 18.8 (CCH_3), 35.3 (SiCHC_2), 38.4 (SiNCH_3), 38.9 (SiNCH_3), 45.7 (CNCH_3), 55.1 (OCH_3), 61.2 (CCH_2N), 114.0 (*C*-3/*C*-5, $C_6H_4OCH_3$), 129.9 (*C*-2/*C*-6, $C_6H_4OCH_3$), 136.1 (*C*-1, $C_6H_4OCH_3$), 158.0 (*C*-4, $C_6H_4OCH_3$). ^{29}Si NMR ([D$_8$]THF): δ −5.4. Anal. Calcd for $C_{18}H_{35}N_3OSi$: C, 64.04; H, 10.45; N, 12.45. Found: C, 64.3; H, 10.2; N, 12.7.

Crystal Structure Analyses. Suitable single crystals of **4** and **10** were isolated directly from the recrystallized products (see above). Suitable single crystals of **5** were obtained from an undercooled (20 °C) melt of this compound (1.29 g) after addition of 2 drops of *n*-hexane; the resulting mixture was kept at 20 °C for 16 h to afford colorless crystals (mp 45−46 °C). The single crystals were mounted in inert oil on a glass fiber and were then transferred to the cold nitrogen gas stream of the diffractometer (Stoe IPDS; graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å)). The structures were solved by direct methods.[10] All non-hydrogen atoms were refined anisotropically.[11] A riding model was employed in the refinement of the hydrogen atoms.

(9) As **9** does not dissolve in *n*-hexane at ambient temperature, heating is required.

(10) (a) Sheldrick, G. M. SHELXS-97; University of Göttingen, Göttingen, Germany, 1997. (b) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **1990**, *46*, 467−473.

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Supporting Information Available: Tables of atomic coordinates and equivalent isotropic displacement parameters, anisotropic displacement parameters, experimental details of the X-ray diffraction studies, and bond lengths and angles of **4**, **5**, and **10**. This material is available free of charge via the Internet at http://pubs.acs.org. In addition, crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as Supplementary Publication Nos. CCDC-245662 (**4**), CCDC-245663 (**5**), and CCDC-245664 (**10**). Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax, (+44) 1223/336033; e-mail, deposit@ccdc.cam.ac.uk).

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(11) Sheldrick, G. M. SHELXL-97; University of Göttingen, Göttingen, Germany, 1997.